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REMARKS

Claims 1 and 13-32 are pending. Support for the amendments to claim 1 can be found at page 4, lines 15, 17 and 37 of the specification.

Claims 1, 13-17, 21-26 and 28-32 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Brant et al. (WO 93/12151) and Holtcamp et al. (U.S. 6,476,166 B1). Applicants respectfully traverse this rejection.

Brant et al. discloses high molecular weight copolymers having from 10 to 100 carbon atoms (see, e.g., Abstract). Brant et al. gives no indication that shorter α -olefins, as presently claimed, can be prepared. Additionally, amended claim 1 is limited to a copolymer with a polydispersity M_w/M_n from 2 to 10 and M_n above 150,000 g/mol. In other words, M_w is at least 300,000 g/mol. None of Brant et al.'s working examples disclose such copolymers. Applicants again enclose Soga et al., *Macromol. Chem. Phys.*, 195, 1369-1379, 1994, with the relevant portions underlined. It is again urged that Brant et al. at best teaches the desirability of copolymers having such high molecular weight, but not how to make them. In particular, applicants urge that Brant et al. does not teach maintaining a high molecular weight and CDBI when the amount of comonomer is increased.

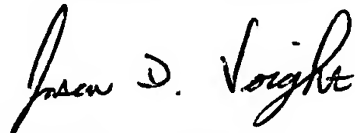
Holtcamp et al. also does not disclose or suggest the claimed copolymers. Applicants urge that the Examiner's speculation that one would use less or eliminate hydrogen during polymerization to maximize molecular weight is unsupported by motivation or suggestion in the cited art. In Holtcamp et al.'s Example 22, more hydrogen and less comonomer is added than in Example 23. Nevertheless, the M_n of

MIHAN et al., Ser. No. 10/069,438

both examples is about the same, which leads to the conclusion that the molecular weight lowering effect must be attributed to the fact that more comonomer was present in Example 23, which also resulted in a decrease in the molecular weight. The effect of the higher comonomer concentration is even more pronounced on the M_w , which drops significantly in Example 23. Therefore, these examples explicitly show, that the more comonomer is added, the lower the molecular weight. The copolymerizations of Examples 1 and 2, columns 13 and 14 were carried out with another catalyst, using no hydrogen. The M_n was below 20,000 g/mol. Therefore, Holtcamp et al. does not teach the inventive polymers.

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Respectfully submitted,
KEIL & WEINKAUF

A handwritten signature in black ink, reading "Jason D. Voight". The signature is written in a cursive style with a large, stylized "V".

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Copolymerization of olefins with SiO_2 , Al_2O_3 , and MgCl_2 -supported metallocene catalysts activated by trialkylaluminiums

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SUMMARY

Copolymerization of ethylene with propene, of ethylene with 1-hexene and of propene with 1-hexene were carried out at 40°C under atmospheric pressure with SiO_2 , Al_2O_3 , and MgCl_2 -supported metallocene catalysts using common alkylaluminiums as cocatalysts. From a detailed analysis of copolymers by ^{13}C NMR, all the copolymers obtained were found to be random ($r_1, r_2 \leq 1$). When ethylene was used as a base monomer, the polymer yield markedly increased with increasing comonomer concentration. The molecular weight of the copolymers obtained in this study were found to be much higher than those obtained with homogeneous Kaminsky-Saun catalysts. Whereas, the polydispersity (M_w/M_n) of the copolymers is dependent on the combination of monomers as well as on the inorganic compounds used as carrier.

Introduction

Copolymers of ethylene with higher olefins like propene, 1-butene, 1-hexene etc. are of great importance in the polyolefin industry¹. Much effort has been paid, therefore, to develop more efficient catalysts which afford tailored copolymers².

Kaminsky et al. found that the homogeneous metallocene-MAO (methylaluminoxane) catalyst system can polymerize various kinds of olefins in extremely high yields³⁻⁵. In contrast to the ordinary heterogeneous Ziegler-Natta catalysts⁶⁻¹¹, the catalyst gives very random copolymers¹².

We have recently reported that the Al_2O_3 - and MgCl_2 -supported zirconocene catalysts combined with common alkylaluminiums promote not only ethylene but also propene polymerizations with a fairly good activity¹³. The SiO_2 -supported zirconocene catalysts can be also activated by common alkylaluminiums when the silicagel is pretreated with a small amount of MAO¹⁴. It may be useful to develop novel heterogeneous catalysts which afford random copolymers. From such a viewpoint, we have applied these supported zirconocene catalysts for the copolymerization of olefins.

Experimental part

Materials

Toluene and propene commercially obtained from Takasago Chemical Co. Ltd. were purified according to the usual procedures¹⁵. $\gamma\text{-Al}_2\text{O}_3$ (from Nippon Co., Ltd.) was calcinated at 400°C

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for 5 h. Anhydrous $MgCl_2$ was donated from Toho Titanium Co., Ltd. SiO_2 (from Fuji Davison Co., Ltd. No. 952) was calcinated at 400°C for 6 h. $Et[IndH_2]_2ZrCl_2$ ($Et = \text{ethylene, Ind} = \text{indenyl}$) was prepared according to the literature¹¹. $Al(CH_3)_3$, $Al(i-C_4H_9)_3$, and methylaluminoxane (MAO) were donated from Toho Akzo Co., Ltd. and used without further purification. All the supported catalysts used in this study were prepared according to the previous reports^{10,11,14}.

Copolymerization procedure

Copolymerizations were conducted at 40°C in a 0.2 dm³ glass reactor equipped with a magnetic stirrer. In case of ethylene/propene copolymerization, the mixture of ethylene and propene was continuously supplied to keep both partial pressures unchanged during the copolymerization. In the copolymerization with 1-hexene as a comonomer, ethylene or propene was continuously supplied to a toluene solution containing 1-hexene. Copolymerization was started by the addition of a catalyst and a supported catalyst and terminated by pouring the reaction mixture into a large amount of dilute hydrochloric acid solution in methanol. The copolymer obtained was adequately washed with methanol and dried *in vacuo* at 60°C for 8 h.

Characterization of copolymers

The molecular-weight distributions (MWD) of the polymers were measured at 145°C by gel permeation chromatography (GPC) (Waters 150C) using *o*-dichlorobenzene as solvent. The compositions of copolymers were determined by ¹³C NMR according to the literature^{11,15}. The ¹³C NMR spectrum was recorded at 120°C using a JEOL OX-270 NMR spectrometer operating at 67.8 MHz. The polymers were dissolved in 1,2,4-trichlorobenzene/benzene-*d*₆ (vol. ratio 9/1) up to 10 wt.-%. The monomer sequence distributions of the copolymers were estimated from the ¹³C NMR spectrum as well as from the Fineman-Ross plots¹⁶.

Results and discussion

Copolymerizations with $Et[IndH_2]_2ZrCl_2/MAO/SiO_2-Al(i-C_4H_9)_3$ as catalyst system

Ethylene/propene copolymerization: Copolymerization of ethylene with propene was first conducted at 40°C under atmospheric pressure with the catalyst system $Et[IndH_2]_2ZrCl_2/MAO/SiO_2-Al(i-C_4H_9)_3$ by changing the monomer feed ratio. The results of this copolymerization are summarized in Tab. 1. It is reported that the apparent polymerization activity with the homogeneous Kaminsky-Sinn catalyst does not change so much by the addition of a comonomer¹⁹. The polymer yield obtained here, however, was found to increase drastically with increasing monomer feed ratio of propene/ethylene up to a high concentration of propene. On the other hand, the molecular weights of the copolymers were much bigger as compared with those previously obtained with the corresponding homogeneous catalyst¹⁹. We have already observed that the polymer particles become much bigger when the polymerization is carried out using the supported catalysts²⁰. The diffusion rates of the monomers as well as alkylaluminum (transfer reagent) to the polymerization centers through the polymer films might be dependent on the crystallinity and thickness of the polymer films. The crystallinity of the polymer films is considered to become much lower with

Copolymerization of olefins with...

Tab. 1. Results of the ethylene/propene copolymerization with $Et[IndH_2]_2ZrCl_2/MAO/SiO_2-Al(i-C_4H_9)_3$ ^{a)}

Run No	Monomer conc. in mol/dm ³		Yield in g	Propene content in polymer ^{b)} in mol-%		$\bar{M}_n \cdot 10^{-3}$	\bar{M}_w/\bar{M}_n ^{c)}
	ethylene	propene					
1	0.10	0	0.49	0	51.1	2.8	
2	0.090	0.053	1.80	8.5	19.7	4.5	
3	0.083	0.088	3.15	13.7	11.7	3.0	
4	0.050	0.26	4.81	51.7	19.4	3.9	
5	0	0.33	1.12	100.0	8.9	2.1	

^{a)} Conditions: catalyst = 100 mg; toluene = 150 cm³; $Al(i-C_4H_9)_3 = 1.5$ mmol at 40°C; 1 atm for 10 min.

^{b)} Calculated from ¹³C NMR.

^{c)} \bar{M}_n : number average molecular weight; \bar{M}_w/\bar{M}_n : ratio of weight- to number-average molecular weight.

increasing comonomer content. The results shown in Tab. 1, i.e., increase of polymer yield and decrease of molecular weight with increasing comonomer feed ratio, may be well understood in terms of such a simple model. However, a more detailed study is necessary to discuss a precise mechanism.

Tab. 2 shows the monomer sequence distributions of the copolymers. The monomer reactivity ratios estimated from ¹³C NMR spectra and Fineman-Ross plots were approximately $r_E = 6.3$, $r_P = 0.12$ and hence $r_E \cdot r_P = 0.8$, which are in fairly good agreement with the values previously obtained with the homogeneous catalyst system $Et[IndH_2]_2ZrCl_2/MAO$ ^{21,22}. It may be concluded from these results that we can produce a random poly(ethylene-co-propene) even by using the heterogeneous catalyst system $Et[IndH_2]_2ZrCl_2/MAO/SiO_2-Al(i-C_4H_9)_3$.

Ethylene/1-hexene and propene/1-hexene copolymerization: Copolymerizations of ethylene with 1-hexene and of propene with 1-hexene were then conducted with the catalyst system $Et[IndH_2]_2ZrCl_2/MAO/SiO_2-Al(i-C_4H_9)_3$ at 40°C under atmospheric pressure by changing the monomer feed ratio, the results of which are summarized in Tabs. 3, 4, 5 and 6. The apparent polymerization activity again increased with increasing 1-hexene concentration. Whereas, the polymer yield did not change so much when propene, which gives polymers with a very low crystallinity, was used as a basic monomer. The monomer reactivity ratios estimated from ¹³C NMR spectra as well as Fineman-Ross plots were $r_E = 22.4$, $r_H = 0.03$ and $r_P = 2.9$, $r_H = 0.3$ and hence $r_E \cdot r_H = 0.7$, $r_P \cdot r_H = 0.9$. These values are also in fairly good agreement with those obtained with the homogeneous $Et[IndH_2]_2ZrCl_2/MAO$ catalyst system. The molecular weights of poly(ethylene-co-(1-hexene)) and poly(propene-co-(1-hexene)) obtained with the catalyst system $Et[IndH_2]_2ZrCl_2/MAO/SiO_2-Al(i-C_4H_9)_3$ were found to be much higher than those produced with the homogeneous catalyst system $Et[IndH_2]_2ZrCl_2/MAO$. With increasing comonomer content, the molecular weights

a) Conditions: catalyst = 100 mg, toluene = 150 cm³, Al(i-C₄H₉)₃ = 1.5 mmol at 40 °C, 1 atm
 b) Calculated from ¹³C NMR for 30 min
 c) Conditions: catalyst = 100 mg, toluene = 150 cm³, Al(i-C₄H₉)₃ = 1.5 mmol at 40 °C for 5 h.

Run No.	Monomer conc. in mol/dm ³	Yield in g	1-Hexene content in polymer ^{b)} in mol-%	$\bar{M}_n \cdot 10^{-3}$	\bar{M}_w/\bar{M}_n
5	0.53	0	1.12	0	2.14
11	0.53	0.050	1.02	3.2	2.06
12	0.53	0.11	1.20	4.8	2.75
13	0.53	0.22	1.17	15.0	2.66
14	0.53	0.45	1.16	28.7	2.74
10 ^{a)}	0	2.49	100.0	5.7	3.94

Tab. 3. Results of propene/1-hexene copolymerization with Et(IndH)₂ZrCl₂/MAO/SiO₂-Al(i-C₄H₉)₃

a) r_1, r_2 : Monomer reactivity ratios of ethylene and 1-hexene, resp.

Run No.	[BHE] [BHE]	[HEH] [HEH]	[HEE] [HEE]	[EEH] [EEH]	[EHE] [EHE]	r_1	r_2	r_1	r_2	r_1	r_2	Fineman-Ross
1	0	0	0	0	0	0	0	0	0	0	0	—
6	4.2	0	0	0	0	8.4	87.4	91.6	8.4	0	21.7	—
7	7.8	0	0	0	0	15.5	76.7	84.4	15.6	0	21.5	—
8	16.9	0	0	0	0	33.7	49.5	66.3	33.7	0	15.8	—
9	19.5	0	0	0	0	34.1	29.6	46.6	46.6	0	19.2	—
10	0	9.2	0	0	0	0	29.6	46.6	46.6	0	19.2	—
average	19.6	0.019	0.4	0	0	100	4.6	100	4.6	0	19.2	—

Tab. 4. Monomer sequence distributions of poly(ethylene-co-1-hexene)

a) Conditions: catalyst = 50 mg, toluene = 150 cm³, Al(i-C₄H₉)₃ = 1.5 mmol at 40 °C, 1 atm
 b) Calculated from ¹³C NMR for 30 min
 c) Conditions: catalyst = 100 mg, toluene = 150 cm³, Al(i-C₄H₉)₃ = 1.5 mmol at 40 °C for 5 h.

Run No.	Monomer conc. in mol/dm ³	Yield in g	1-Hexene content in polymer ^{b)} in mol-%	$\bar{M}_n \cdot 10^{-3}$	\bar{M}_w/\bar{M}_n
1	0.10	0	0.16	0	2.79
6	0.10	0.10	0.61	4.2	3.05
7	0.10	0.20	1.17	7.8	3.91
8	0.10	1.57	16.9	29.7	3.91
9	0.10	1.95	26.3	26.3	2.19
10 ^{a)}	0	2.49	100.0	5.7	3.94

Tab. 5. Results of ethylene/1-hexene copolymerization with Et(IndH)₂ZrCl₂/MAO/SiO₂-Al(i-C₄H₉)₃

a) r_1, r_2 : Monomer reactivity ratios of ethylene and propene, resp.

Run No.	[PEE] [PEE]	[PEP] [PEP]	[PEE] [PEE]	[PEP] [PEP]	[PEE] [PEE]	[PEP] [PEP]	r_1	r_2	r_1	r_2	Fineman-Ross
1	0	0	0	0	0	0	0	0	0	0	—
2	6.9	1.6	0.0	0.6	13.4	77.5	84.2	15.0	0.8	6.7	—
3	10.5	3.2	0.0	1.4	18.2	66.7	75.8	22.6	1.6	7.6	—
4	17.9	21.1	12.7	9.6	23.0	15.7	27.2	49.6	6.8	23.2	—
5	0	0	0	0	0	0	0	0	0	100	—
average	7.0	0.15	1.0	0	0	0	100	4.6	100	4.6	—

Tab. 6. Monomer sequence distributions of poly(ethylene-co-propene)

Tab. 6. Monomer sequence distributions of poly(propylene-co-(1-hexene))

Run. No.	[PII] (%)	[PII] (HP)	[HH] (%)	¹³ C NMR				Fingerman-Ross	
				$\tau_H^{(1)}$	$\tau_H^{(2)}$	$\tau_H^{(3)}$	$\tau_H^{(4)}$	τ_H	$\tau_H^{(5)}$
5	100	0	0	—	—	—	—	—	—
11	93.5	6.5	0	2.76	—	—	—	—	—
2	90.3	9.7	0	1.91	—	—	2.9	0.30	0.9
3	72.2	25.6	6.5	2.35	0.41	1.0	—	—	—
4	51.3	39.9	8.8	2.20	0.53	1.1	—	—	—
0	0	0	100	—	—	—	—	—	—
			average	2.81	0.47	1.1			

r_p, r_M : Monomer reactivity ratios of propene and 1-hexene, resp.

of poly[ethylene-co-(1-hexene)] decreased to some extent, while that of poly(propene-co-(1-butene)) remained almost unchanged. These tendencies can be explained in terms of the model proposed above in the copolymerization of ethylene and propene.

Copolymerizations with $\text{Et/IndH}_2\text{ZrCl}_2/\text{MAO}/\text{MgCl}_2-\text{Al}(\text{CH}_3)_3$ and $\text{Et/IndH}_2\text{ZrCl}_2/\text{Al}_2\text{O}_3-\text{Al}(\text{iC}_4\text{H}_9)_3$ as catalyst systems

Copolymerizations of ethylene with propene and 1-hexene were conducted under similar conditions by changing the catalyst carrier from SiO_2 to MgCl_2 and Al_2O_3 . When copolymerization was conducted with the catalyst $\text{Et}(\text{IndH}_2)_2\text{ZrCl}_2/\text{MgCl}_2$ using $\text{Al}(\text{iC}_4\text{H}_9)_3$ as cocatalyst, the resulting polymer displayed a considerably strong peak at around 125°C in addition to the strong peak attributed to the copolymer, indicating that an appreciable amount of polyethylene is produced as by-product. It may be plausible to consider that $\text{Al}(\text{iC}_4\text{H}_9)_2\text{Cl}_n$ ($n = 1$ or 2) is produced by the reaction of $\text{Al}(\text{iC}_4\text{H}_9)_3$ with MgCl_2 . Therefore, the active species formed between $\text{Et}(\text{IndH}_2)_2\text{ZrCl}_2/\text{MgCl}_2$ and $\text{Al}(\text{iC}_4\text{H}_9)_3$ might be responsible for the homopolymerization of ethylene. In fact, only homopolyethylene was obtained, when the copolymerization of ethylene with propene was carried out with the catalyst system $\text{Et}(\text{IndH}_2)_2\text{ZrCl}_2/\text{MgCl}_2-\text{Al}(\text{iC}_4\text{H}_9)_2\text{Cl}$. On the other hand, when $\text{Al}(\text{CH}_3)_3$ was used as cocatalyst, no detectable amount of polyethylene was produced. From such a viewpoint, copolymerization was conducted using $\text{Al}(\text{CH}_3)_3$ as cocatalyst, the results of which are summarized in Tabs. 7 and 8. The molecular weights of poly(ethylene-co-propene) were not so different from those obtained with the catalyst system $\text{Et}(\text{IndH}_2)_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2-\text{Al}(\text{iC}_4\text{H}_9)_3$. The monomer reactivity ratios estimated from Fineman-Ross plots were $r_E = 10.5$, $r_P = 0.06$ and hence $r_E \cdot r_P = 0.6$, indicating that the copolymer is also random but the comonomer (propene)-

Tab. 7. Results of ethylene/propene copolymerization with $\text{Et}(\text{Ind})\text{Hf}_2\text{Cl}_2/\text{MgCl}_2-\text{Al}(\text{CH}_3)_3$

Run	Monomer conc. in mol/dm ³	Yield in %	Propene content in polymer ^(b)	$M_n \cdot 10^{-3}$	M_w/M_n
5	0.00	0	0	58.4	3.6
6	0.090	0.57	0.58	48.7	3.5
7	0.083	0.085	0.72	41.9	2.9
8	0.075	0.13	1.20	37.2	2.8
9	0.050	1.53	32.2	16.1	3.2
10	0	0.34	100	4.1	3.5

Conditions: $\text{Et}[(\text{IndH}_4)_2\text{ZrCl}_2] = 2.4 \cdot 10^{-2} \text{ mmol}$, solvent = 150 cm^3 , $\text{Al}(\text{CH}_3)_3 = 10 \text{ mmol}$
at $+60^\circ \text{C}$, 1 atm for 1 h
Calculated from ^{13}C NMR.
Conditions: $\text{Et}[(\text{IndH}_4)_2\text{ZrCl}_2] = 6.7 \cdot 10^{-2} \text{ mmol}$, solvent = 150 cm^3 , $\text{Al}(\text{CH}_3)_3 = 10 \text{ mmol}$
at $+40^\circ \text{C}$, 1 atm for 1 h.

Tab. 6. Monomer sequence distributions of poly(1,3-butadiene-co-propene) obtained with EtLiNH_4 , ZnCl_2 , MgCl_2 , AlEtCl_2 .

[illegible]

Fig. 1. Monomer reactivity ratios of ethylene and propene, resp.

Tab. 9. Results of ethylene/1-hexene copolymerization with $\text{Et}[\text{IndH}_4]_2\text{ZrCl}_2/\text{MgCl}_2$ - $\text{Al}(\text{CH}_3)_3$

Run.	Monomer conc. in mol/dm ³	Yield in %	1-Hexene content in polymer ^a in mol-%	$M_n \cdot 10^{-3}$	M_w/M_n
15	0.10	0	0	58.4	5.6
21	0.10	0.10	2.1	22.1	9.3
22	0.10	0.20	3.8	16.5	9.2
23	0.10	0.54	7.6	19.1	6.1
24	0.10	1.00	18.8	12.3	5.8

Conditions: Et₃N, 120°C, 1 atm for 1 h.
Calculated from 11C NMR.

Tab. 10. Monomer sequence distributions of poly[styrene-co-(1-borne)] with $\text{Et}[\text{IndHf}(\text{I})_2\text{ZrCl}_2/\text{MgCl}_2\text{-Al}(\text{CH}_3)_3]$

[illegible]

^a B, H: Monomer reactivity ratios of ethylene and 1-hexene, resp.

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Tab 12. Monomer sequence distributions of poly(ethylene-co-propene) obtained with $\text{Et}(\text{InH}_2)_2\text{ZrCl}_2/\text{Al}_2\text{O}_3$ - $\text{Al}(\text{i-C}_4\text{H}_9)_3$.

[illegible]

^a ρ : Monomer reactivity ratios of ethylene and propene, resp.

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